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(54) IMPROVEMENTS IN POLYCARBONATE COPOLYMERS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, residing at 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel polycarbonate copolymer derived from bis-(3,5-dimethyl - 4 - hydroxy - phenyl) sulfone, and to a method of preparing the copolymer.

Previously it has been known to prepare aromatic carbonate homopolymer resin by reacting 2,2 bis - (4,4' hydroxy - phenyl) propane with phosgene. The resulting polycarbonate is not suitable for the preparation of textile fibers. It does not crystallize readily enough or to a sufficient extent to gain dry cleaning solvent resistance. Additionally, it undergoes some hydrolytic degradation when washed in alkaline media, and the stick temperature is too low for convenient ironing.

The present invention provides a process for the production of a carbonate copolymer, which comprises reacting (1) bis - (3,5 - dimethyl - 4 - hydroxy - phenyl) sulfone, (2) a bisphenol other than said sulfone and (3) a carbonate precursor as herein defined, the amounts of starting material (1) and (2) being such that the molar proportion of the residues corresponding to (1) and (2) in the resulting copolymer is not less than 1.

The present invention also provides a copolymer consisting of the reaction product of (1) bis - (3,5 - dimethyl - 4 - hydroxyphenyl) sulfone, (2) a bisphenol other than said sulfone and (3) a carbonate precursor as herein defined, wherein the reaction mixture of monomers (1) and (2) initially consist of 60—99 weight % of the bis - (3,5 - dimethyl - 4-hydroxyphenyl) sulfone and, correspondingly, 40—1 weight % of the bisphenol based on the total weight of monomers (1) and (2).

The compounds of the present invention can be used to produce orientable textile fibers having high heat distortion temperatures.

Heretofore, it has been known to prepare copolymers of a bisphenol and a dihydroxy diphenyl sulfone as described in U.S. patent 3,271,376, but the the copolymers of the present invention have not been previously described. The present copolymers possess high melting temperatures, excellent solvent resistance and enhanced hydrolytic stability. Fibers and films prepared from these copolymers may be oriented over a wide temperature range. Oriented fibers exhibit outstanding tenacity.

The copolymers of this invention may be prepared by reacting 60—99 weight percent of a bis - (3,5 - dimethyl - 4 - hydroxyphenyl) sulfone, and correspondingly 40—1 weight % of another bisphenol, with a carbonate precursor. As shown in the following examples, when employing less than 60 weight % of the particular dihydroxy diphenyl sulfone, the resulting copolymer has poor hydrolytic stability and lower heat distortion temperature.

The copolymers of this invention are soluble in such solvents as, for example, chloroform, tetrachloroethane, ortho dichlorobenzene or methylene chloride. Low concentration solutions of the copolymer of this invention can be prepared at room temperature. Higher concentrations, particularly where the dihydroxy diphenyl sulfone content is high, may require using a heated or hot solvent.

The bis(hydroxybenzene) employed in the practice of this invention can be any bisphenol other than the dihydroxy diphenyl sulfone employed herein to prepare the copolymer. Examples of some of the bis(hydroxybenzenes) are bis - (4 - hydroxyphenyl) methane, 2,2 bis (4 - hydroxyphenyl) propane [which is the preferred bis(hydroxybenzene)] and 4,4 bis-

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(4-hydroxyphenyl) heptane; dihydric phenol ethers such as bis - (4 - hydroxyphenyl) ether and bis - (3,5 dichloro - 4 - hydroxydiphenyl) ether; dihydroxy diphenyls such as p,p'-dihydroxy diphenyl and 3,3' - dichloro 4,4' dihydroxy diphenyl.

As used herein the term "carbonate precursor" designates a carbonyl halide, such as carbonyl bromide, carbonyl chloride and, carbonyl fluoride, or mixtures thereof; carbonate esters such as diphenyl carbonate, di-(chlorophenyl) carbonate, di-(bromophenyl) carbonate, di-(trichlorophenyl) carbonate, di-(tribromophenyl) carbonate, di-(tolyl) carbonate, di-(naphthyl) carbonate, di-(chloronaphthyl) carbonate, phenyl tolyl carbonate and chlorophenyl chloronaphthyl carbonate, or mixtures thereof; and bishaloformates of dihydric phenols (such as the bischloroformate of hydroquinone) or glycols (such as the bishaloformates of ethylene glycol, neopentyl glycol and polyethylene glycol). The preferred carbonate precursor is carbonyl chloride. The said carbonate esters are used as carbonate precursors in an ester exchange type of reaction with the bisphenol.

The reaction for preparing the copolymer when employing either a carbonyl halide or a bishaloformate is carried out in the presence of an acid acceptor, which acid acceptor may be either an organic or an inorganic compound. In addition, the reaction may be carried out in the presence of an organic or an aqueous medium. The organic acid acceptor as used herein can be, e.g., a tertiary amine and include such materials as pyridine, triethylamine, dimethylaniline or tributylamine. When employing an inorganic acid acceptor, one may use either a hydroxide, a carbonate, a bicarbonate or a phosphate of an alkali or alkaline earth metal.

The following examples are set forth to illustrate more clearly the principle and practice of this invention to those skilled in the art. Unless otherwise specified, where parts are mentioned, they are parts by weight.

EXAMPLE I

To a reaction vessel fitted with a stirrer, 1.5 grams of 2,2 bis - (4 - hydroxyphenyl) propane (known as bisphenol-A) and 13.5 grams of bis - (3,5 dimethyl - 4 - hydroxyphenyl) sulfone are added. The flask contains 25 ml. of pyridine and 100 ml of methylene chloride. Phosgene is then bubbled through the mixture at a rate of about 0.5 grams per minute at room temperature and atmospheric pressure for a period of about 30 minutes. The reaction is stopped and the resin is precipitated by slowly adding to the reaction mixture, a 1:1 mixture of acetone and methanol while maintaining vigorous agitation. A stringy precipitate is formed.

The resulting copolymer is soluble in hot tetrachloroethane (100°C) and upon preparing a film cast from a solution thereof a colorless, transparent tough film is formed. Upon placing the film in an oven at 250°C for a period of approximately ten hours, no color or dimensional change is noticed.

EXAMPLES II—VI

Example I is repeated and in each case with the weight % of the bis - (3,5 - dimethyl-4-hydroxyphenyl) sulfone and bisphenol-A being in the feed mixture of the two as indicated with the following results:

Example	Wt. % of sulfone	Wt. % of bisphenol—A	Hydrolytic stability as weight loss after 70 hours in 10% NAOH solution at 80°C.	Tensile heat distortion temp. at 75 psig stress
II	92	8	minor	246°C
III	84	16	18.7	244
IV	76	24	18.3	224
V	60	40	27.9	227
Control A	40	60	56.8	198
Control B	0	100	87.0	165

EXAMPLE VI

The copolymer of Example III is dissolved in methylene chloride to prepare a 15% solution thereof; the solution is spun into a textile fiber by the wet spinning process using methanol in the spin bath. The fibre is taken up at 100 ft. per minute. The fiber is dried at 100°C for about 24 hours.

EXAMPLE VII

The fiber so produced in Example VI is oriented to various degrees by drawing the fiber over a hot stage at various temperatures. The following results are obtained:

Draw ratio	Draw Temperature	Denier	Tenacity grams/denier @ room temp.	Elongation prior to breaking @ room temp.
3:1	190°C	27.9	3.5	22.5%
3.5:1	190	26.8	4.3	17.5
4:1	235	23.2	4.8	14.6
5:1	290	19.5	4.7	64.0
As spun		100.0	0.7	6.0

From this example, it can be seen that the fibers have a very broad temperature of orientation and that the fiber oriented at the highest temperature has the highest elongation at room temperature.

U.K. patent specification No. 808,486 claims high molecular weight thermoplastic polycarbonates containing residues of 2,2'-, 3,3' or 4,4'-dihydroxydiphenyl-sulphone, or of 4,4' - dihydroxy - 2,2'- or 3,3' - dimethyl-diphenyl-sulphone, or of 2,2'-dihydroxy-4,4'-dimethyl-diphenyl-sulphone, or of 2,2'-dihydroxy-1,1'-dinaphthyl-sulphone, alone or together with residues of aliphatic, cycloaliphatic or other aromatic dihydroxy compound.

WHAT WE CLAIM IS:—

1. A copolymer consisting of the reaction product of (1) bis-(3,5 dimethyl-4-hydroxyphenyl) sulfone, (2) a bisphenol other than said sulfone and (3) a carbonate precursor as herein defined, wherein the reaction mixture of monomers (1) and (2) initially consist of 60—99 weight % of the bis - (3,5 dimethyl - 4-hydroxyphenyl) sulfone and, correspondingly, 40—1 weight % of the bisphenol based on the total weight of monomers (1) and (2).

2. A copolymer according to Claim 1, wherein the bisphenol is 2,2 bis-(4,4'-hydroxyphenyl) propane.

3. A copolymer according to Claim 1 or 2, wherein the carbonate precursor is phosgene.

4. A copolymer substantially as herein described with reference to any one of Examples I to V.

5. A process for the production of a carbonate copolymer which comprises reacting (1) bis - (3,5 - dimethyl - 4 - hydroxyphenyl) sulfone, (2) a bisphenol other than said sulfone and (3) a carbonate precursor as herein defined, the amounts of starting material (1) and (2) being such that the molar proportion of the residues corresponding to (1) and (2) in the resulting copolymer is not less than 1.

6. A process according to Claim 5, wherein the carbonate precursor is phosgene.

7. A process for the production of a carbonate copolymer substantially as herein described with reference to any one of Examples I to V.

8. A carbonate copolymer whenever produced by the process claimed in Claim 7.

9. An orientable textile fiber obtained from a copolymer as claimed in any one of Claims 1—4 and 8.

10. A fiber according to Claim 9 substantially as herein described in Example VI.

11. An oriented textile fiber obtained by drawing a fiber of a copolymer claimed in any one of Claims 1—4 and 8.

12. A fiber according to Claim 11 substantially as herein described with reference to Example VII.

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